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# THE EFFECT OF DECAY ON THE CHEMICAL COMPOSITION OF WOOD

## I. ACTION OF TRAMETES PINI ON DOUGLAS FIR

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Forest Products Laboratory, Forest Service
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# THE EFFECT OF DECAY ON THE CHEMICAL COMPOSITION OF WOOD

## I. ACTION OF TRAMETES PINI ON DOUGLAS FIR

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It is known that wood partially destroyed by fungi shows differences in chemical composition as compared with sound wood, and it seems probable that different chemical constituents of the wood tissue are consumed in the biological evolution of different fungi. The most common aspect of this process is, that fungi consume the carbohydrates (pentosans, cellulose and other carbohydrates which might be present) of the wood leaving behind the lignin. In some cases, however, it is believed that the growing fungus consumes the lignin and leaves behind a white fibrous material which is assumed to be pure cellulose. Except in some cases this assumption was based on microscopical experiments conducted on the remaining white fibers which gave certain stain tests usually ascribed to cellulose. A. C. Thaysen and H. J. Bunker[2] mention in their book several times that, for instance, Trametes pini Brot. (white pocket rot) and Fomes igniarius Linn. (false tinder fungus) decompose the lignin and leave behind patches

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[1] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

[2] A. C. Thaysen & H. J. Bunker, "The Microbiology of Cellulose, Hemicellulose, Pectins and Gums," Oxford University Press, London (1927).

of white or whitish cellulose. This statement for _Fomes igniarius_ is based on the experiments of H. VonSchrenk and P. Spaulding,[3] who identified the cellulose by Schultze's chloriodide-zinc reaction. No chemical analysis of the affected wood has been made by them. As Schultze's reaction is not specific for cellulose,[4] it is not surprising that B. Johnson and R. W. Hovey[5] by chemical analysis of aspen wood affected with _Fomes igniarius_ came to an opposite conclusion; the cellulose content decreased 37.4 per cent, and the lignin content increased 67.4 per cent in the decayed wood as compared with the sound wood. (These figures are calculated on the cellulose or lignin basis respectively.) But even this chemical analysis does not decidedly solve the question whether _Fomes igniarius_ consumes lignin or cellulose or both. B. Johnson and R. W. Hovey give the lignin content in the sound aspen wood, as determined by the concentrated $H_2SO_4$ method to be 7.86 per cent, which is extremely low. It neither checks with analyses of aspen carried out by different authors independently nor does it approach by far the lignin content of any other known species.

I would expect F. igniarius to leave an excess
of cellulose

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[3] H. VonSchrenk & P. Spaulding, Diseases of Deciduous Trees, U. S. Dept. Agr. Bull. 149, 34 (1909).

[4] Compare: L. F. Hawley & L. E. Wise, Chemistry of Wood, Chem. Catalog Co., N. Y. (1926), p. 233 and following; K. Hess, Chemie der Cellulose, Leipzig (1928), p. 246.

[5] B. Johnson and R. W. Hovey, J. Soc. Chem. Ind. 37, T. 132 (1918); Pulp & Paper Mag. 16, 85 (1918).

of white or whitish cellulose. This statement for *Fomes igniarius* is based on the observations of H. Von Schrenk and P. Spaulding,[2] who identified the cellulose by Schultze's chloriodide-zinc reaction. No chemical analysis of the affected wood has been made by them. As Schultze's reaction is not specific for cellulose,[4] it is not surprising that E. Johnson and R. W. Hovey[5] by chemical analysis of aspen wood affected with *Fomes igniarius* came to an opposite conclusion; the cellulose content decreased 27.6 per cent, and the lignin content increased 67.4 per cent in the decayed wood as compared with the sound wood. (These figures are calculated on the cellulose or lignin basis respectively.) But even this chemical analysis does not decidedly solve the question whether *Fomes igniarius* consumes lignin or cellulose or both. E. Johnson and R. W. Hovey give the lignin content in the sound aspen wood, as determined by the concentrated $H_2SO_4$ method to be 7.88 per cent, which is extremely low. It neither checks with analyses of aspen carried out by different authors independently nor does it approach by far the lignin content of any other known species.

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[2] H. Von Schrenk & P. Spaulding, Diseases of Deciduous Trees, U. S. Dept. Agr. Bull. 149, 34 (1909).

[4] Compare: L. F. Hawley & L. E. Wise, Chemistry of Wood, Chem. Catalog Co., N. Y. (1926), p. 225 and following; E. Heuser, Chemie der Cellulose, Leipzig (1927), p. 540.

[5] E. Johnson and R. W. Hovey, J. Soc. Chem. Ind. 37, T. 132 (1918); Pulp & Paper Mag. 16, 95 (1918).

C. G. Schwalbe and E. Becker[6] found the lignin content determined by the $H_2SO_4$ method to be 18.24 per cent, which reasonably checks with the values for other hardwood species. O. Kress and his coworkers[7] give the lignin content of aspen as 26.6 per cent, Bray and Andrews[8] 23.4 per cent. We must, therefore, assume that error was made in the lignin determination of Johnson and Hovey and that the question whether Fomes igniarius consumes lignin or cellulose is still open. Falck and Haag[9] published data of analyses of wood decayed by Polyporus annosus and Merulius domesticus. Their exact data seem to prove decidedly that Polyporus annosus belongs to the white rot fungi and consumes mainly lignin whereas Merulius domesticus is of the brown rot type consuming mainly the carbohydrates of the wood. This aspect on the Merulius decay has been substantiated by a detailed analysis of wood attacked by Merulius lacrymans carried out by Barton-Wright and Boswell.[10]

For Trametes pini so far no chemical analysis of affected wood has been published.[11] B. Johnson and H. N. Lee,[12]

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6 C. G. Schwalbe and E. Becker, Z. angew. Chem. 32, 229 (1919).

7 "Control of Decay in Pulp and Pulpwood" by O. Kress, C. J. Humphrey, C. A. Richards, M. W. Bray and J. A. Staidl, U.S.D.A. Bull. 1298, p. 23 (1925).

8 M. W. Bray and T. M. Andrews, Paper Trade Jour. May 10, 1923; Paper-Ind. July (1923).

9 Richard Falck and Walter Haag. B. 225-232 (1927).

10 E. C. Barton-Wright and J. S. Boswell, Biochem. J. 33, 110-114 (1929).

11 Recently P. M. Soum, Bull. Inst. du Pin, Bordeaux No. 64, p. 257, published results of an analysis of pine wood with Trametes pini decay. His paper will be reviewed later.

12 B. Johnson and H. N. Lee, Pulp and Paper Magazine 21, 111 (1923).

however, mention that according to unpublished data of J. L. Parsons[13] the "decay of wood caused by Trametes pini resulted in an increase in cellulose content of 15 per cent and a decrease in lignin of 30 per cent." Since further details are not published, no comparison of the methods applied and the results obtained can be accomplished. It seemed, therefore, desirable to undertake a chemical analysis of a wood specimen which showed white pocket rot decay to a high degree. This report covers analyses carried out on such naturally decayed wood. Experiments with artificially-infected wood are under way.

## Experimental Part

The tested wood material was Douglas fir which showed a high degree of decay in the heartwood and apparently no decay in the sapwood as is usually found in natural conditions with Trametes pini (Plate I). The parts which were most affected were separated from the unaffected ones and both were collected separately. Moreover, the white fibers were separated from the white pockets in order to show any pronounced differences in chemical composition. Thus, three different samples were obtained showing three steps in the decay: (a) the apparently sound wood, (b) the partly decayed wood, and (c) the white fibers from the pockets. Care was taken to secure in all cases wood only from the heartwood. Sample (c) did not represent the pure fibers, as they exist in the pockets, but was a mixture consisting of these fibers and less destroyed wooden parts, because it was impossible to separate them in a pure state mechanically. This sample, however,

[13] J. L. Parsons, Hammermill Paper Co., Erie, Pa.

Plate I

may be considered as containing a high concentration of white fibers.

Table 1.--Chemical differences in three steps of decay of Douglas fir caused by *Trametes pini*

| | Sound wood | Partly decayed wood | Highly decayed wood |
|---|---|---|---|
| | Per cent | Per cent | Per cent |
| Moisture | 4.95 | 5.77 | 5.66 |
| Ash | 0.17 | 0.25 | -- |
| Cold water | 5.82 | 3.48 | -- |
| Hot water | 1.51 | 2.39 | -- |
| 1 per cent alkali | 19.01 | 19.79 | -- |
| Ether | 2.79 | 1.23 | -- |
| Benzene/alcohol | 5.00 | 1.90 | -- |
| Lignin | 29.95 | 27.20 | 22.36 |
| Cellulose | 52.17 | 55.24 | 59.96 |
| Alpha cellulose | 35.73 | 35.66 | -- |
| Beta cellulose | 0.84 | 1.09 | -- |
| Gamma cellulose | 15.60 | 18.49 | -- |
| Acetic acid | 0.86 | 0.62 | -- |
| Total pentosans | 9.34 | 8.52 | -- |
| Pentosans in cellulose | 3.53 | 2.93 | -- |
| Total methoxyl | 4.79 | 4.32 | -- |
| Methoxyl in lignin | 4.19 | 3.83 | -- |

The three samples were separately cut into sawdust and the material collected on a 60/80-mesh screen was used for analysis. The methods of analysis were those adopted in the Forest Products Laboratory, as they are compiled by Mark W. Bray.[14] A slight change was made in the cellulose determination where the revised method of Ritter was applied.[15] The

[14] Mark W. Bray, Paper Trade Jour. Dec. 20, 1928.
[15] G. J. Ritter, Ind. & Eng. Chem. 16, 947 (1924).

cellulose was not bleached but after washing with hot water it was dried and weighed. The results obtained are shown in Table 1. This table shows that the lignin content in the two steps of decay decreases, viz. (calculated on the lignin basis) 9.18 per cent in the partly decayed and 24.34 per cent in the highly decayed samples. The cellulose content increases correspondingly, viz. (calculated on the cellulose basis) 5.90 per cent and 14.95 per cent, respectively, as compared with the sound wood. The latter values of both lignin and cellulose check reasonably with those mentioned by Johnson and Lee.[16]

Soum recently[17] published a paper where he states that _Trametes pini_ attacks particularly the cellulose leaving behind the lignin, so that finally the cellulose is found to be 21.67 per cent instead of 56.00 and the lignin 57.15 per cent instead of 32.23 per cent, as based on the oven-dry wood after decay. Soum's samples gave also lignin reactions.[18] As Soum gives no details whatever of his work and his samples were naturally decayed, it is more probable that besides the identified _Trametes pini_ other fungi were in the analyzed sample (from the chemical data it appears that brown rot fungi were acting) and that the chemical changes were mainly due to these other fungi. In any case, our results do not check with those of Soum but indicate that _Trametes pini_ belongs to the white rot fungi, Falck's "destruction" type of decay.
corrosion

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16 loc. cit.
17 loc. cit.
18 It is not stated which lignin reactions are meant.

The presentation of our results in the form of Table 1 does not give the true picture of the decay process. We find, for instance, an increase in the cellulose and the ash content, a fact which has to be explained by a greater decrease in the weight of the decaying wood sample than of those two constituents. The analyses were calculated on the oven-dry basis of the analyzed samples and not on the sound wood. In order to overcome this difficulty and to obtain a better picture of the decay, we might assume that the cellulose has been left unattacked and unchanged. Recalculating Table 1 on this basis, we obtain Table 2. This table gives a better idea of the probable effect of decay. The decrease in the lignin content, the most important effect, amounts (as calculated on the lignin basis,) to 14.2 per cent in the partly decayed wood and to 33 per cent in the totally decomposed sample as compared with the sound wood. Parallel to this effect the decrease in the methoxyl content of the affected sawdust, amounting to 18.5 per cent on the methoxyl basis is also noted. The difference in the lignin and methoxyl decrease is satisfactorily explained by the fact that the decay affected even the nature of the lignin itself. We find, therefore, the methoxyl content of the lignin isolated from rotten wood to be less than that from sound wood.[19]

All extractives except those in hot water are lower in the case of decayed wood. It seems plausible to assume that

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[19] A similar fact is reported by M. W. Bray and T. M. Andrews, J. Ind. & Eng. Chem. 16, (1924), and Fischer, Schrader & Friedrich, Ges. Abh. Kenntnis Kohle 5, 530 (1920).

Table 3.--Effect of Trametes pini (Brot.) on Douglas fir recalculated on unchanged cellulose

Basis from Table 1

| | Sound wood | Partly decayed wood | Total decayed wood |
|---|---|---|---|
| | Per cent | Per cent | Per cent |
| Moisture | 4.95 | 5.45 | 4.93 |
| Ash | 0.17 | 0.24 | |
| Cold water extract | 5.82 | 3.29 | |
| Hot water extract | 1.51 | 2.26 | |
| 1 per cent alkali | 19.01 | 18.69 | |
| Ether | 2.79 | 1.16 | |
| Benzene alcohol | 5.00 | 1.78 | |
| Lignin | 29.95 | 25.69 | 19.46 |
| Cellulose | 52.17 | 52.17 | 52.17 |
| Alpha cellulose | 35.73 | 33.68 | |
| Beta cellulose | 0.84 | 1.03 | |
| Gamma cellulose | 15.60 | 17.46 | |
| Acetic acid | 0.36 | 0.59 | |
| Total pentosans | 9.34 | 8.05 | |
| Pentosans in cellulose | 3.53 | 2.77 | |
| Total methoxyl | 4.79 | 3.99 | |
| Methoxyl in lignin | 4.19 | 3.62 | |

All figures calculated on oven-dry sawdust basis, and recalculated on unchanged cellulose basis.

the fungus consumes not only lignin, but also extractives. This assumption is further substantiated by the loss of pentosans during this decay, which almost entirely are the pentosans in cellulose.[20] Extraction with hot water causes a partial hydrolysis of the decayed cellulose which, as will be seen later, is less resistant than that of sound wood. This explains the higher yield of extractives found with hot water.

As mentioned, cellulose obtained from decayed wood is less stable than that of sound wood. The yield of beta and gamma cellulose is higher, that of alpha cellulose lower in the case of cellulose obtained from decayed wood. Such facts have been found by other authors in the case of decay[21] and from our unpublished results obtained on cellulose from hydrolysed sawdust, the same effect is evident. Summarizing, it seems that Trametes pini consumes largely lignin and extractives, and in its final stage also cellulose, after converting it by a kind of hydrolysis in an easily soluble material. That Trametes pini consumes also cellulose can be seen on wood pieces affected by it. In some pockets the isolated cellulose is visible. In some it has been entirely consumed. (Plate I.) Black spots indicate holes caused by the fungus.

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[20] Hawley, Fleck and Richards, "Effect of Decay on the Chemical Composition of Wood," Ind. Eng. Chem. May (1928).

[21] U. S. Dept. Bull. 1298, loc. cit., M. W. Bray and J. A. Staidl, etc.

From the differences in the chemical nature of cellulose from sound and decayed wood, it is evident that our assumption of unattacked and unchanged cellulose is not right. It is very probable that some of the cellulose has been already consumed, as can be seen from the ash content increase. An exact answer to this question will be furnished by the investigations on artificially infected wood which are under way.

## Microscopical Study

Although it is known that color reactions of both lignin and cellulose are not specific for them yet a study of such reactions was made as they might throw a light on the nature of the white fibers isolated by the decay. It was found that all tests, viz., the phloroglucinol test[22] and the Cross and Bevan test[23] with the ferric chloride-ferricyanide did not give the expected lignin color on the fibers isolated by the fungus. On the other hand, Schulze's chloriodide zinc test[24] gave the cellulose test on the isolated fibers by the decay and did not give the test on the sound wood. It has to be mentioned that all these tests have been made on sections similar to those given in Plates II and III, where part of the fibers are isolated and part of them still kept together by the lignin. The color tests appeared to be in the wood part or in the cellulose part, respectively, when lignin or cellulose tests were made.

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[22] J. Wiesner, Sitzungsber der Wiener. Akad. Wiss. 77, I. 60 (1878).

[23] C. F. Cross and E. J. Bevan, Cellulose. Longmans, Green & Co., London (1918), p. 124.

[24] Cf. L. Radlkofer, Annalen, 94, 332 (1855) and C. V. Wisselingh, J. Bot. 31, 624 (1897).

Plate II

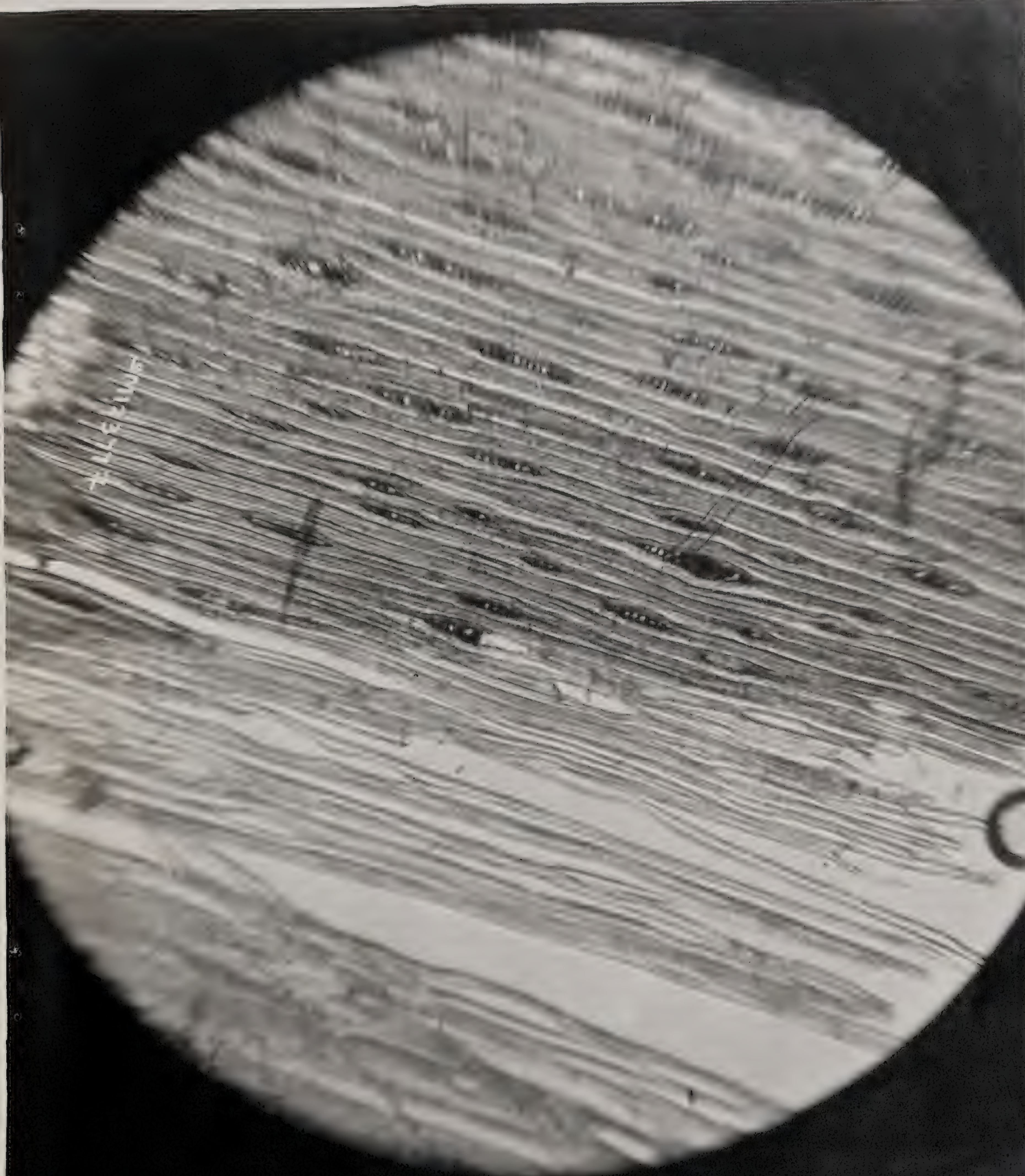
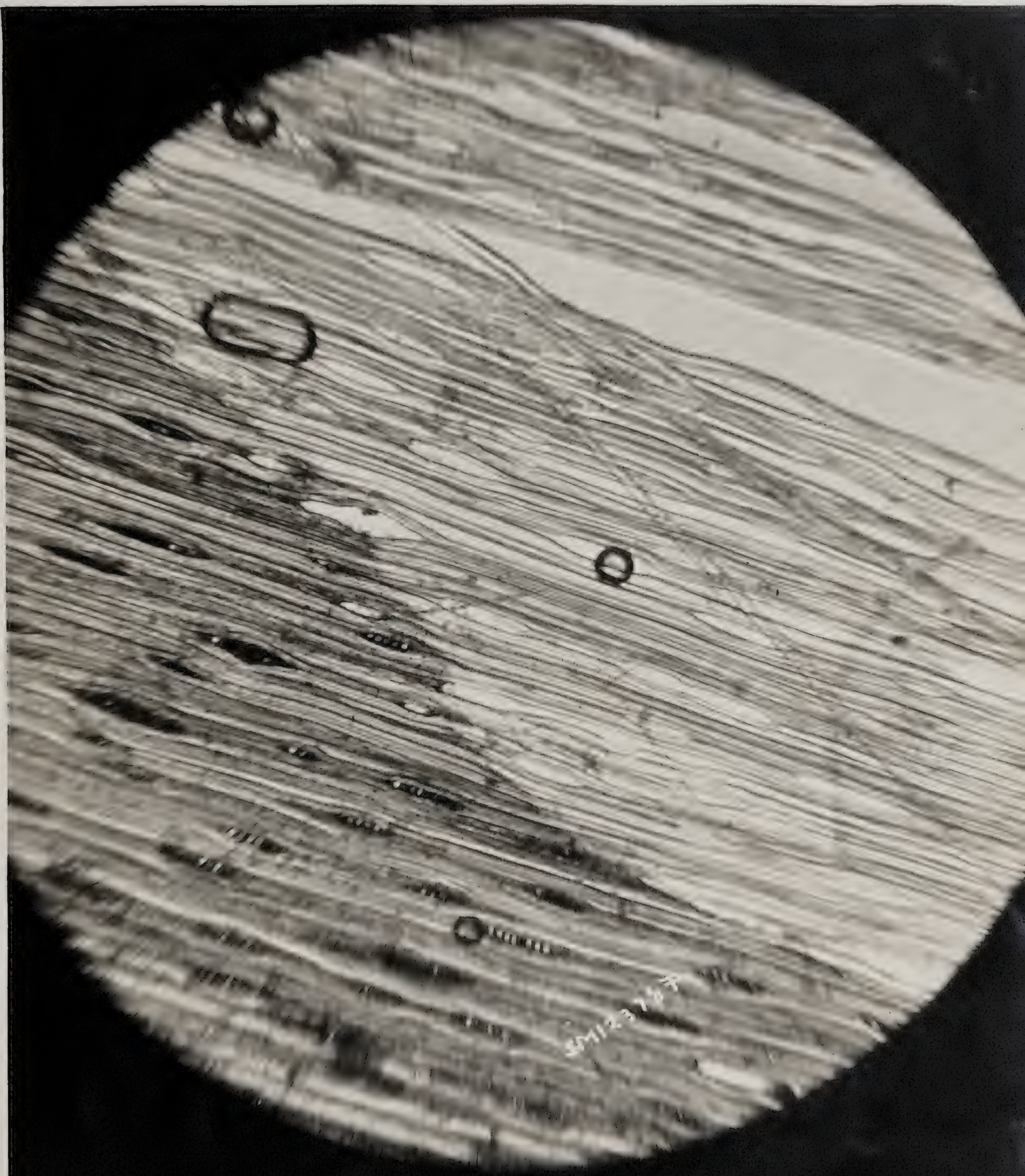


Plate III



Plates II and III represent photomicrographs of sections made from decayed wood magnified 250 X. The sections are unstained. The darker side is the less decayed part of wood which had still the natural color of the wood and when stained gives the lignin colors as mentioned above. It is to be noticed that these fibers stick together and show the same structure as the wood itself. The brighter part shows the white fibers isolated by the fungus which gave the cellulose stain test. It is interesting that the darker medullary rays which are still visible in the unaffected part on both plates are entirely consumed by the fungus in the brighter part. Plate II shows even in the center one ray partly consumed and partly conserved. It is known that also in the pulping process the medullary rays are entirely destroyed. They seem therefore to be the less resistant part of the cellulosic wood structure. The cellulose fibers in the brighter part which are loosened by the fungus due to removal of the cementing lignin show, when at higher magnification, the known microstructure of the cell fiber. A possible assumption that they might be the fungus hyphae is therefore disproved.

Although this chemical and microscopical analysis is not entirely satisfactory, since only an analysis on the weight basis would yield reliable data, yet there seems to be little doubt that <u>Trametes pini</u> causes in its development the described effects.